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(54) BROMINE CONTAINING FLUOROPOLYMER

(71) We, E.I. DU PONT DE NEMOURS AND COMPANY, a corporation organized and existing under the laws of the State of Delaware, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to fluoropolymers including non-elastomeric fluoropolymers and elastomeric fluoropolymers (fluoroelastomers).

In the industries which manufacture and use fluoroelastomers and fluoropolymer plastics, there is a need for polymeric materials of this type which are easy and economical to cure (cross-link or vulcanize). This is especially true in applications where it is desired to obtain a product having good resistance to damage by heat, solvents, and /or corrosive chemicals. Good creep-resistance is also often important.

According to the invention, we provide a fluoropolymer which includes interpolymerized units of

(a) up to 3 mole %, based on the total moles of components (a) and (b), of units derived from bromotrifluoroethylene or 4-bromo-3,3,4,4-tetrafluorobutene-1, with the proviso that enough of such units are present to provide at least 0.05 weight % bromine in the copolymer, and

(b) enough units derived from alternative components (b-1), (b-2) or (b-3) as follows to make up the remainder of the copolymer:

(b-1) tetrafluoroethylene and a perfluoroalkyl perfluorovinyl ether wherein the perfluoroalkyl group contains 1-5 carbon atoms,

(b-2) 45-65 mole % tetrafluoroethylene, 20-55 mole % of a C₂ - C₄ olefinic hydrocarbon and from 0 to 30 mole % vinylidene fluoride, or

(b-3) vinylidene fluoride, at least one fluorine-containing olefin copolymerizable therewith, and optionally said perfluoroalkyl perfluorovinyl ether, said olefin being a compound which contains 2-7 carbon atoms, contains no bromine atom, and contains at least as many fluorine atoms as carbon atoms.

In the fluoropolymer of the invention, it is often preferred that enough of the component (a) units are present in the copolymer to provide 0.3 - 1.5 weight % bromine in the copolymer. An especially preferred component (a) compound is bromotrifluoroethylene. It will be noted that items (a) and (b) are components in the sense that they are ingredients (in copolymerized form) of the fluoropolymer.

In some of the preferred embodiments of the invention, the novel copolymer is a fluoroelastomer wherein component (b) is composed of units derived from 50-80 mole % tetrafluoroethylene and 20-50 mole % perfluoroalkyl perfluorovinyl ether. Thus, a monomer combination referred to above as (b-1) is used to make this copolymer. Said ether compound is preferably perfluoromethyl perfluorovinyl ether.

In other preferred embodiments, the copolymer is a fluoropolymer (preferably a fluoroelastomer) wherein component (b) is composed of units derived from any one of the following three combinations:

(i) vinylidene fluoride and hexafluoropropylene or pentafluoropropylene; or
(ii) vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or pentafluoropropylene; or

(iii) vinylidene fluoride, said perfluoroalkyl perfluorovinyl ether, and hexafluoro-

propylene and/or tetrafluoroethylene.

Thus, in making this class of copolymers, one uses a monomer combination within what is referred to above as (b-3). In such embodiments, component (b) can, for example, be composed of 30-70% vinylidene fluoride units and 30-70% hexafluoropropylene units (units derived from these compounds) based on the weight of component (b). Or component (b) can be composed of 25-70 weight % vinylidene fluoride units, 19-60 weight % hexafluoropropylene units and 3-35 weight % tetrafluoroethylene units. Or components (b) can be composed of units derived from (on a weight % basis) 4-15% of tetrafluoroethylene, 48-65% of vinylidene fluoride, 8-23% of hexafluoropropylene and 17-30% of a perfluoroalkyl perfluorovinyl ether wherein the alkyl group contains 1-5 carbon atoms. Or component (b) can be composed of units derived from (on a mole % basis) 10-85% vinylidene fluoride, 2-50% of said perfluoroalkyl perfluorovinyl ether and 3-80% of hexafluoropropylene and/or tetrafluoroethylene. One can also use chlorotrifluoroethylene as the fluorine-containing olefin of component (b-3).

To illustrate preferred embodiments of the monomer combination referred to above as (b-2), the copolymer can be a fluoroelastomer wherein component (b) is composed of 45-55 mole % of tetrafluoroethylene units and 45-55 mole % propylene units. Or wherein component (b) is composed of 50-65 mole % of tetrafluoroethylene units, 5-26 mole % of vinylidene fluoride units and 20-45 mole % of propylene units. In the latter, the propylene can be replaced with any of the following: butene-1, a mixture of 0.1-5.0 mole % of ethylene or isobutylene and 50-99.9 mole % of propylene or butene-1, and a mixture of about 50 mole % of ethylene and 50 mole % of isobutylene.

In preparing the fluoropolymer of the invention it is preferred that the reaction mixture of monomer components also contains a free-radical initiator, and the copolymer-forming reaction is carried out as a free radical emulsion polymerization reaction. Among the most useful free-radical initiators to use in such a reaction are ammonium persulfate, sodium persulfate, potassium persulfate, or a mixture of two or more such compounds. Also useful are other water-soluble inorganic peroxide compounds, for example sodium, potassium, and ammonium perphosphates, perborates, and percarbonates. The initiator can be used in combination with a reducing agent such as sodium, potassium, or ammonium sulfite, bisulfite, metabisulfite, hyposulfite, thiosulfate, phosphite, or hypophosphite, or in combination with a ferrous, cuprous, or silver salt, or other easily oxidized metal compound. Known organic free-radical initiators can also be used, preferably in combination with a suitable surfactant such as sodium lauryl sulfate or ammonium perfluorooctanoate. The surfactant can be selected from those known to be useful in the manufacture of fluoropolymers. A surfactant can of course also be present when using an inorganic initiator. A suitable known chain transfer agent can also be present during the emulsion polymerization reaction, but in many cases this is not preferred.

After completion of the preferred emulsion polymerization reaction, the copolymer can be isolated from the resulting polymer latex by known methods, for example by coagulation by adding an electrolyte or by freezing, followed by centrifuging or filtering and then drying the copolymer.

The copolymer-forming reaction can also be carried out in bulk, or in an organic liquid containing an organic free-radical initiator. It is usually preferred that none of the organic liquid present is a chain transfer agent.

During preparation of the copolymer, the reaction mixture is preferably heated in a reactor which has been flushed with an inert gas at 50-130°C, under superatmospheric pressure, for example under a pressure of 7-140 kg./cm.², preferably 35-105 kg./cm.². In some of the most useful procedures, the polymerization is carried out as a continuous process and the reaction mixture has an average residence time in the reactor of 5 to 30 minutes in some cases and up to 2 or 3 hours in others. Residence time can be calculated by dividing the reactor volume by the volume of latex produced per hour.

The fluoropolymer of the invention in the majority of cases will have an inherent viscosity of 0.01 deciliters/gram or higher, with special preference for an inherent viscosity of 0.2-1.2 deciliters/gram. Inherent viscosity of some of the fluoropolymers can be measured at 30°C at a copolymer concentration of 0.1% by weight in a solvent composed of 87% by volume of tetrahydrofuran and 13% by volume of N,N-dimethylformamide. A test method using a different solvent is described below in Example 1.

One skilled in the art will have no difficulty in preparing various fluoropolymers useful in the practice of the present invention. For example, he will realize after reading the present disclosure that substantially the same polymer-forming methods can be used as are described by Rexford in U.S. 3,051,677, By Pailthorp and Schroeder in U.S. 2,968,649, by Sianesi et al in U.S. 3,331,823 and U.S. 3,335,106, by Albin and Gallagher in U.S. 3,235,537, by Brasen and Cleaver in U.S. 3,467,635 and by other inventors whose patents concern the preparation of fluoropolymers.

Polymers in accordance with the invention may be used in the formulation of fluoropolymer compositions which may be used in the manufacture of cured fluoropolymer articles. Thus a fluoropolymer composition may comprise a polymer in accordance with the invention in admixture with from 0.5 to 10% by weight (based on the weight of the copolymer) of an organic peroxide.

Such fluoropolymer compositions and their preparation and use are described and claimed in our copending Application No. 15252/78 (Serial Patent No. 1,528,342).

Fluoropolymers in accordance with the invention possess generally advantageous properties that make them suitable for a wide variety of different applications. Thus they can (a) be cured rapidly; (b) be cured at atmospheric pressure to a non-porous or non-spongy structure, an important advantage in the manufacture of fluoropolymer-coated wire and fluoropolymer hose; (c) be cured at about ordinary room temperature; (d) undergo a surprisingly great increase in torque during the ODR cure test described below, which is desirable in many applications; (e) have lower (i.e. more useful) compression set values after curing than prior art diamine-cured fluoroelastomers (this applies to certain fluoroelastomer compositions of the present invention wherein the fluoroelastomer is a vinylidene fluoride copolymer) and (f) be cured with less tendency to undergo polymer degradation than certain prior art fluoroelastomer materials cured with a blend of aromatic hydroxy compound and quaternary phosphonium compound of the type shown by Patel et al in U.S. 3,712,877. (This applies to compositions based upon vinylidene fluoride copolymers in accordance with this invention which contain units derived from a perfluoroalkyl perfluorovinyl ether).

The following examples illustrate the invention; all amounts are by weight unless otherwise indicated. Inherent viscosities referred to in the Examples are expressed as deciliters/gram.

Example 1

A curable fluoropolymer of this invention in the form of an elastomeric copolymer of tetrafluoroethylene, perfluoromethyl perfluorovinyl ether and bromotrifluoroethylene is prepared by a continuous process composed of the following operations:

(1) Continuously feeding the three monomers described below in (i.e. the polymerization reaction zone) which has been flushed with nitrogen, while operating the stirrer of the reactor at 500 rpm nitrogen, while operating the stirrer of the reactor at 500 rpm for thorough mixing of the reactor contents, and while the contents of the reactor are heated at 70°C, under a pressure of 42 kg./cm.² so that the reaction mixture formed in operation

(2) Below will undergo an emulsion polymerization reaction as it passes through the reactor, the reactor residence time being about 2.7 hours based on the ratio of the 3.8 liter reactor to the emulsion output rate of about 1.4 liters per hour, the monomers and the feed rate for each being as shown below in Table I;

(3) During operation 1, constantly feeding to the reactor through a first metering pump during each hour a solution composed of 6.38 grams of ammonium persulfate, 4.5 grams of dibasic sodium phosphate heptahydrate and 12.0 grams of ammonium perfluoro octanoate dissolved in 600 ml. of water (distilled), and simultaneously feeding to the reactor through a second metering pump during each hour a solution composed of 5.25 grams of sodium sulfite dissolved in 600 ml. of water, the reaction mixture being maintained at a pH of 6.1;

(4) Continuously removing from the reactor the resulting copolymer latex which is continuously formed during operations 1 and 2, the latex being passed first through a back-pressure regulating valve set to maintain the desired reactor pressure of 42 kg./cm.², and then through a sealed container from which the off-gas (unreacted monomers) is led to a gas chromatograph where its composition is determined and recorded in Table I below;

(5) After discarding the latex obtained during the first four residence times, collecting the desired quantity of latex and mixing it for uniformity, the latex having a pH of about 6.1 and a copolymer solids content of 26.0%; and

(6) Isolating the resulting copolymer from the latex by the gradual addition of a 4% aqueous solution of potassium aluminum sulfate until the copolymer is coagulated, washing the copolymer particles with distilled water, removing the water by means of a filter apparatus, and then drying the copolymer in a circulating air-oven at 100°C to a moisture content of less than 1%.

Table I

| | Monomer | Feed g./hr. | Off-Gas g./hr. | Incorporated in Polymer | | |
|----|--------------------------------------|----------------|-------------------|----------------------------|--------------|----|
| | | | | g./hr. | Wt. % Mole % | |
| 5 | Tetrafluoroethylene | 260 | 14 | 246 | 56.0 68.5 | 5 |
| | Perfluoromethyl perfluorovinyl ether | 300 | 117 | 183 | 41.6 30.0 | |
| 10 | Bromotrifluoroethylene | 10 | 1 | 9 | 2.4 1.5 | 10 |
| | Total | 570 | 132 | 438 | | |

The resulting copolymer is an elastomer which can be cured in the manner described in Example 2 of our copending Application No. 15252/78 (Patent No. 1,528,342); as indicated in Table I above, it contains in each 100 grams of polymerized units about 56 grams of polymerized tetrafluoroethylene, 41.6 grams of polymerized perfluoromethyl perfluorovinyl ether and 2.4 grams of bromotrifluoroethylene. The copolymer has an inherent viscosity of 0.38; this property is measured at 30°C at a polymer concentration of 0.2% by weight in a solvent composed of 58% by volume of 2,3,3-trichloroperfluorobutane, 39% by volume of "FC-75" solvent and 3% by volume of diethylene glycol dimethyl ether. The "FC-75" solvent is a perfluoro cyclic ether type of solvent of the empirical formula $C_8F_{16}O$, sold under the 3M Company trade name "FC-75", and described in further detail in the above-mentioned Proskow U.S. Patent 3,740,369. In place of this solvent one can use the product of fluorinating tetrahydrofuran until one obtains a solvent composed predominantly of 2-perfluorobutyl perfluorotetrahydrofuran. The copolymer has a bromine content of 1.2% by weight; and it is insoluble in aliphatic and aromatic hydrocarbons.

One skilled in the art, after reading the present disclosure, will have no difficulty in preparing other copolymers of the present invention in a similar manner to that described in Example 1 when using other proportions of the same three monomers.

Example 2

A curable fluoroelastomer is prepared by repeating Example 1 except the monomer feed rate is adjusted so that a copolymer is obtained which contains 65.0 mole % of tetrafluoroethylene units, 33.5 mole % of perfluoromethyl perfluorovinyl ether units and 1.5 mole % of bromotrifluoroethylene units. The resulting Example 2 copolymer has the same bromine content and inherent viscosity as the Example 1 copolymer.

A curable fluoroelastomer composition may be prepared from this copolymer using the procedure described in Example 2 of our copending Application No. 15252/78 (Patent No. 1,528,342).

Example 3

A curable fluoroelastomer is prepared in the manner described in Example 2 except that the monomer feed rate is adjusted so that a copolymer is obtained which contains 65.6 mole % tetrafluoroethylene units, 33.0 mole % perfluoromethyl perfluorovinyl ether units and 1.4 mole % bromotrifluoroethylene units. This copolymer has a bromine content of 0.9 weight % and an inherent viscosity (Example 1 method) of 0.35.

A curable fluoroelastomer composition may be prepared from this copolymer using the procedure described in Example 3 of our copending Application No. 15252/78 (Patent No. 1,528,341).

Example 4

A fluoroelastomer of the present invention is prepared by repeating Example 1 except: The monomers fed to the reactor in the present Example are 56 parts vinylidene fluoride, 44 parts hexafluoropropylene and 0.8 part bromotrifluoroethylene; a two-liter reactor is used; the pressure in the reactor is 63 kg./cm.²; the reaction mixture temperature is 105°C and the pH is 3.3; the reactor residence time is about 15 minutes; and operation (2) consists of feeding to the reactor (for each 100 parts of monomer) 400 parts water containing 0.3 part of ammonium persulfate and 0.05 part sodium hydroxide. The gas chromatograph of operation (3) can be omitted. The copolymer obtained, after 91% monomer conversion, contains 59.1% vinylidene fluoride units, 40% hexafluoropropylene units and 0.9% bromotrifluoroethylene units (weight %). The latex has a copolymer solids content of 18.7%.

The resulting fluoroelastomer has a Mooney viscosity of 94 at 100°C; this measure of bulk viscosity is determined on a Mooney viscometer using the large rotor and a ten-minute shearing time.

The curable fluoroelastomer composition may be prepared from this copolymer using the procedure described in Example 9 of our copending Application No. 15252/78 (Patent No. 1,528,342).

Example 5

A curable non-elastomeric fluoropolymer is prepared as follows: A copolymer which contains about 98% vinylidene fluoride units, 1.7% bromotrifluoroethylene units and a small amount of polymerized hexafluoropropylene units is made by repeating Example 4 except the copolymer is prepared by feeding to the reactor 100 parts vinylidene fluoride, 35 parts hexafluoropropylene, 1.6 parts bromotrifluoroethylene and (for each 100 parts vinylidene fluoride) 454 parts water containing 0.45 part ammonium persulfate, 0.09 part sodium hydroxide and 0.94 part ammonium perfluoro octanoate; the reactor pressure is 42 kg./cm.²; residence time is 30 minutes; the hexafluoropropylene feed is discontinued after polymerization is well established and the reaction is allowed to continue in the absence of hexafluoropropylene for 75 minutes. The copolymer is dried in a vacuum oven for 14 hours at 70°C. It has a bromine content of 0.85 weight %.

Example 6

A fluoropolymer which is a rubbery plastic is prepared by repeating Example 4 except the copolymer is made from 69 parts vinylidene fluoride, 11 parts hexafluoropropylene, 19 parts tetrafluoroethylene and 1 part bromotrifluoroethylene, and (for each 100 parts of monomer) 400 parts water containing 0.85 part ammonium persulfate and 0.21 part sodium hydroxide. The reaction mixture pH is 4.6, residence time is 15 minutes and the latex copolymer solids content (after 96% monomer conversion) is 19.7%. The copolymer contains 70% vinylidene fluoride, 9% hexafluoropropylene, 20% tetrafluoroethylene and 1% bromotrifluoroethylene (weight %). The portion of the copolymer which dissolves (80%) has an inherent viscosity of 0.46 when measured at 30°C at a concentration of 0.1% by weight in a solvent composed of 87% by volume of tetrahydrofuran and 13% by volume of N,N-dimethylformamide.

A curable fluoropolymer composition may be prepared from this copolymer using the procedure described in Example 12 of our copending Application No. 15252/78 (Patent No. 1,528,342).

Example 7

A fluoropolymer is prepared as described in Example 4 except the copolymer is made from 77 parts tetrafluoroethylene, 23 parts propylene, 1.1 part bromotrifluoroethylene and (for each 100 parts of monomer) 359 parts of water containing 2.87 parts of surfactant (a 33% aqueous solution of sodium lauryl sulfate), 1.65 parts ammonium persulfate and 1.08 parts sodium hydroxide. The reaction conditions: Pressure of 42 kg./cm.², temperature of 80°C, residence time of 3 hours and pH of 9.0. The latex copolymer solids content (after 87% monomer conversion) is 20.7%. The copolymer contains about 73.4% tetrafluoroethylene, 25.3% propylene and 1.3% bromotrifluoroethylene (by weight). It has a Mooney viscosity of 61 (Example 4 method).

A curable fluoropolymer composition may be prepared from this copolymer using the procedure described in Example 13 of our copending Application No. 15252/78 (Patent No. 1,528,342).

Example 8

A fluoropolymer is prepared as described in Example 7 except the copolymer is made from 68 parts tetrafluoroethylene, 18.3 parts vinylidene fluoride, 13.1 parts propylene, 0.67 part bromotrifluoroethylene and (per 100 parts of monomer) 343 parts water containing 3.1 parts of the Example 7 surfactant, 1.96 parts ammonium persulfate and 1.37 parts sodium hydroxide. Residence time is 90 minutes. The latex copolymer solids content (after 67% monomer conversion) is 17.8%. The copolymer contains about 68.6% tetrafluoroethylene, 12.9% vinylidene fluoride, 17.5% propylene and 1.0% bromotrifluoroethylene.

A curable fluoropolymer composition may be prepared from this copolymer using the procedure described in Example 14 of our copending Application No. 15252/78 (Patent No. 1,528,342).

Example 9

A fluoropolymer is prepared by repeating Example 4 except the copolymer is made from 46 parts vinylidene fluoride, 51 parts hexafluoropropylene, 41 parts tetrafluoroethylene, 12 parts bromotrifluoroethylene and (for each 140 parts monomer) 600 parts water containing 0.59 part ammonium persulfate and 0.15 part sodium hydroxide. The reaction mixture pH is 2.9, residence time is 20 minutes, and the latex copolymer solids content (after 91.2% monomer conversion) is 17.7%. The copolymer contains 36% vinylidene fluoride, 31% hexafluoropropylene, 32% tetrafluoroethylene and 1% bromotrifluoroethylene (weight % of polymerized units).

A curable fluoropolymer composition may be prepared from this copolymer using the procedure described in Example 16 of our copending Application No. 15252/78 (Patent No. 1,528,342).

WHAT WE CLAIM IS:-

1. A fluoropolymer which includes interpolymerized units of

- (a) up to 3 mole %, based on the total moles of components (a) and (b), of units derived from bromotrifluoroethylene or 4-bromo-3,3,4,4-tetrafluorobutene-1, with the proviso that enough of such units are present to provide at least 0.05 weight % bromine in the copolymer, and
- 5 (b) enough units derived from alternative components (b-1), (b-2) or (b-3) as follows to make up the remainder of the copolymer: 5
- (b-1) tetrafluoroethylene and a perfluoroalkyl perfluorovinyl ether wherein the perfluoroalkyl group contains 1-5 carbon atoms,
- (b-2) 45-65 mole % tetrafluoroethylene, 20-55 mole % of a C₂ - C₄ olefinic hydrocarbon and from 0 to 30 mole % vinylidene fluoride, or 10
- 10 (b-3) vinylidene fluoride, at least one fluorine-containing olefin copolymerizable therewith, and optionally said perfluoroalkyl perfluorovinyl ether, said olefin being a compound which contains 2-7 carbon atoms, contains no bromine atom, and contains at least as many fluorine atoms as carbon atoms. 10
- 15 2. A polymer as claimed in claim 1 wherein enough component (a) units are present to provide 0.3-1.5 weight % bromine in the copolymer. 15
3. A polymer as claimed in claim 1 or claim 2 wherein component (b) is composed of units derived from 50-80 mole % tetrafluoroethylene and 20-50 mole % of a perfluoroalkyl perfluorovinyl ether.
- 20 4. A polymer as claimed in any of claims 1-3 wherein the ether is perfluoromethyl perfluorovinyl ether. 20
5. A polymer as claimed in any of claims 1-4 wherein component (a) is bromotrifluoroethylene.
6. A polymer as claimed in claim 1 or claim 2 wherein component (b) is composed of units derived from any one of the following three combinations: 25
- 25 (i) vinylidene fluoride and hexafluoropropylene or pentafluoropropylene; or 25
- (ii) vinylidene fluoride, tetrafluoroethylene and hexafluoropropylene or pentafluoropropylene; or
- (iii) vinylidene fluoride, said perfluoroalkyl perfluorovinyl ether, and hexafluoropropylene and/or tetrafluoroethylene. 30
- 30 7. A polymer is claimed in claim 6 wherein component (b) is composed of units derived from 30-70% vinylidene fluoride and 30-70% hexafluoropropylene by weight of (b). 30
8. A polymer as claimed in claim 6 wherein component (b) is composed of units derived from 25-70% vinylidene fluoride, 19-60% hexafluoropropylene and 3-35% tetrafluoroethylene by weight of (b). 35
- 35 9. A polymer as claimed in claim 1 or claim 2 wherein component (b) is composed of 45-55 mole % of tetrafluoroethylene units and 45-55 mole % of propylene units. 35
10. A polymer as claimed in claim 1 or claim 2 wherein component (b) is composed of 50-65 mole % of tetrafluoroethylene units, 5-26 mole % of vinylidene fluoride units and 20-45 mole % of propylene units. 40
- 40 11. A polymer as claimed in any of claims 1-10 which has an inherent viscosity of 0.01 deciliters/gram or higher. 40
12. A polymer as claimed in claim 1 substantially as hereinbefore described.
- 45 13. A polymer as claimed in claim 1 substantially as hereinbefore described with reference to the Examples. 45

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